



Predicting CO₂ solubility in aqueous N-methyldiethanolamine solutions with ePC-SAFT



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ABSTRACT

In this work, electrolyte PC-SAFT equation of state developed in 2005 with the parameters from Held et al. [Chem. Eng. Res. Des. 92 (2014) 2884–2897] has been applied to predict the solubility of CO₂ in aqueous N-methyldiethanolamine (MDEA) solutions. The considered temperature range was 313–413 K, MDEA weight fractions up to 0.32 (related to the binary water/MDEA system) and loadings of up to 1.32 (mole CO₂/mole MDEA).

In order to predict CO₂ solubilities, the reaction equilibria and phase equilibria were solved simultaneously by explicitly accounting for the electrolyte species being present in the system: H⁺, OH⁻, HCO₃⁻, CO₃²⁻ and MDEAH⁺. The pure-component parameters for the molecular components (H₂O, CO₂, MDEA) and for all ions except MDEAH⁺ were already available in the literature. MDEAH⁺ pure-component parameters were inherited from MDEA, and the charge was explicitly accounted for in ePC-SAFT. Binary parameters were applied only for the pairs H₂O/CO₂, H₂O/ions, and H₂O/MDEA. The deviations between experimental and ePC-SAFT modeled CO₂ solubility in aqueous MDEA solutions was 19.82% for a temperature range of 313–413 K, a MDEA weight fractions of 0.19, and CO₂ loadings of up to 1.3 (mole CO₂/mole MDEA). As binary parameters have not been adjusted to experimental CO₂ solubility data in aqueous MDEA solutions, these results can be considered as predictive.

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1. Introduction

In times of global warming, the development of process engineering applications for the reduction of anthropogenic carbon dioxide emission is becoming increasingly important [1]. One possibility to remove CO₂ from process, synthetic or natural gases is the absorption with aqueous alkanolamine solutions. This concept is known since 1930 [2], and from that time on research has started on developing different alkanolamine systems for the use of CO₂ absorption [3]. The big advantage of aqueous amine systems is that the solubility of CO₂ is based on physical absorption and chemical absorption caused by reactions of CO₂ in the liquid phase. In this way, a high loading of the alkanolamine with the absorbate is achieved. Suitable alkanolamines are especially monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). The latter has advantageous properties with respect to the CO₂ load capacity and to chemical and thermal stability. Thus, the industrial relevance of aqueous MDEA solutions

for the purification of gases has continuously increased in the recent years [4].

In the ternary water/CO₂/MDEA system, significant amounts of different ion species are formed caused by reactions in the liquid phase, especially the protonated MDEA (MDEAH⁺) and hydrogen carbonate (HCO₃⁻). Modeling phase equilibria in this ternary water/CO₂/MDEA system requires explicitly accounting for the formation of the ions. This is important as electrolytes have a huge impact on phase equilibria and thermodynamic properties of aqueous systems [5–7]. Modern electrolyte models consider short-range (SR) interactions and long-range (LR) interactions among the charged species in order to describe the residual Helmholtz energy or the excess Gibbs energy of a system. Debye and Hückel proposed already in 1923 their approach for the characterization of dilute electrolyte solutions [8]. The description of the LR forces requires the dielectric constant of an electrolyte solution, which has shown to influence the results obtained with an electrolyte model [9,10].

The CO₂ solubility in aqueous amine solutions has intensively been measured, correlated, and modeled. Among the first approaches to describe experimental data are empirical models [11,12]. However, a huge set of experimental data is required and the application is limited to the range of conditions the parameters

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Nomenclature

Roman symbols

a	Helmholtz free energy per number of molecules (-)
a	Activity (-)
c	Equation constants (-)
d	Temperature-dependent segment diameter (Å)
k_B	Boltzmann constant, 1.38065×10^{-23} J/K (J/K)
k_{ij}	Binary interaction parameter (-)
k_{ij}^{hb}	Binary interaction parameter (-)
K_a	Activity-based equilibrium constant (-)
m^{seg}	Number of segments (-)
n_i	Mole number of component i (-)
N^{assoc}	Number of association sites (-)
NP	Number of data points (-)
p	Pressure (Pa, bar)
R	Ideal gas constant (J/mol/K)
T	Temperature (K)
u/k_B	Dispersion-energy parameter (K)
x	Mole fraction (-)
Z	Real gas factor (-)

Greek symbols

α	CO ₂ loading (mole CO ₂ /mole MDEA)
γ_i	Symmetrical activity coefficient of component i (related to pure component) (-)
γ_i^*	Asymmetrical activity coefficient of component i (related to infinite dilution) (-)
φ_i	Fugacity coefficient of component i (-)
ε_r	Relative dielectric constant (-)
$\varepsilon^{A_i B_i}/k_B$	Association-energy parameter (K)
ϕ	Osmotic coefficient (-)
$\kappa^{A_i B_i}$	Association-volume parameter (-)
λ	Reaction coordination number (mol)
ρ	Number density (1/m ³)
ν	Stoichiometric factor (-)
σ_i	Temperature-independent segment diameter of molecule i (Å)

Subscripts

i, j	Component indices
seg	Segment
0	Pure substance

Superscripts

assoc	Association
disp	Dispersion
exp	Experimental
hc	Hard chain
ion	Ionic
L	Liquid phase
mod	Modeled
res	Residual
V	Vapor phase
+, -	Positive or negative charge
∞	Infinite dilution
*	Related to infinite dilution
0	Pure substance

Abbreviations

ARD	Absolute average relative deviation
CPA	Cubic plus association
DEA	Diethanolamine
EOS	Equation of state

g^E	Excess Gibbs energy
LR	Long range
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
PR	Peng Robinson
SAFT	Statistical associating fluid theory
SR	Short range
VLE	Vapor-liquid equilibria

have been fitted to. In the literature, electrolyte and non-electrolyte models have been developed, which consider SR or SR+LR forces in order to describe aqueous amine+CO₂ solutions. These models describe the excess Gibbs energy ($\rightarrow g^E$ -models) or the Helmholtz energy (\rightarrow equations of state (EOS)) of a system. Austgen et al. [13] and Zhang and Chen [14] modeled aqueous amine solutions and aqueous solutions containing amine mixtures using eNRTL [15]. Faramarazi et al. [16] applied modified UNIQUAC to describe the CO₂ solubility in systems with MEA and MDEA, respectively. Kuranov et al. [17] and Kamps et al. [18] correlated Pitzer parameters [19] to experimental H₂S and CO₂ solubility data in aqueous MDEA solutions in a broad temperature and pressure range. The Pitzer model was further used by Arcis et al. [20] in order to model the VLE and to estimate the solution enthalpy of CO₂ in aqueous MDEA solutions.

The drawback of g^E models is the huge number of adjustable binary parameters, that often depend on temperature and sometimes even on concentrations. The application of EOS usually requires a much smaller number of binary fitting parameters. Zoghi et al. [21] and Avlund et al. [22] applied the CPA EOS in order to model the VLE of aqueous MDEA, MEA, and DEA solutions by explicitly accounting for the complex association behavior. The association behavior can also be described with SAFT-based EOS. Button and Gubbins [23] used SAFT to model the VLE of aqueous MEA and DEA solutions under the presence of CO₂. A big average deviation of 43% was observed, which probably was due to neglecting chemical reactions. This shortcoming was corrected for in the work of Nasrifar and Tafazzol [24]; they used PC-SAFT EOS combined with chemical reaction equilibria in order to model gas solubilities (H₂S, CO₂) in aqueous ethanolamine solutions. In a more recent work, Pahlavanzadeh and Fakouri Baygi [25] applied PC-SAFT combined with chemical reaction equilibria in order to predict CO₂ solubilities in aqueous MDEA solutions. However, Pahlavanzadeh and Fakouri Baygi neglected the presents of any ions in the systems.

Next to these non-electrolyte EOS models, also electrolyte models have been applied in the literature to model gas solubilities in aqueous amine solutions. Such models (e.g., electrolyte Peng-Robinson EOS (PR EOS) [26] and various electrolyte SAFT-based approaches [27–31]) describe the Helmholtz energy of an electrolyte solution by considering SR forces as well as the LR forces (either via the Debye-Hückel theory or via the mean spherical approximation). Most researchers consider electrolytes as fully dissociated into cations and anions requiring ion-specific parameters that account also for ion solvation via SR forces. Based on a non-electrolyte PR-EOS (proposed by Huttenhuis et al. [32]), Zoghi et al. [21] included a theory accounting for LR forces and a Born term to describe the solubility of CO₂ in aqueous solutions of MDEA in wide ranges of concentration, pressure, temperature, and gas loading. However, they used binary interaction parameters that were fitted to the ternary systems. Using this approach, Zoghi et al. could quantitatively describe the solubility of CO₂ in aqueous MDEA solutions.

Although many approaches have been developed and applied so far to model the solubility of CO₂ in aqueous amine solutions,

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